THE INFLUENCE OF CLAY SLURRY INVASION ON THE DISSOLUTION OF SPENT NUCLEAR FUEL UNDER REPOSITORY ENVIRONMENTS

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

SKIN

DELIVERABLE D3.6

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Abstract

In order to evaluate the potential changes on spent nuclear fuel (SNF) dissolution caused by a bentonite slurry during a glacial period, batch experiments were conducted by dissolving crystalized ThO_2 particles (as a simulator of SNF UO_2 matrix) under anoxic conditions, with or without the presence of a synthesised clay (montmorillonite). The results show that, in a neutral pH and CO_2 free water solution, Th concentration reached around ppt level in two months, and increases with decreasing pH and increasing carbonate content. Th(IV) in solution can be sorbed by synthetic montmorillonite. Given that the Th(IV) sorption process is much faster than the ThO_2 dissolution, the Th(IV) concentrations in batch experiments with ThO_2 and clay are much lower than the solubility level of ThO_2. Therefore the quantity of Th(IV) sorbed on the clay in the presence of ThO_2 is much less than the calculated value using K_d value for Th(IV) on montmorillonite and the solubility of Th(IV)oxide.

Introduction

In the KBS-3 repository concept, spent fuel will be encapsulated in copper-cast iron canisters embedded in bentonite clay placed in deep granite bedrock. During a glacial period it has been shown that dilute glacial water may cause erosion of the bentonite clay, followed by severe bentonite losses. When the anoxic glacial melt water reaches the repository, the buffer may be partially or completely eroded, leaving a cavity filled with a slurry of colloidal clay particles. These colloidal clay particles are produced through the erosion of the clay in the tunnel backfill. For a canister breached under such circumstances, the clay particles are not expected to affect the fuel oxidative dissolution rate. Dissolved U(IV) would, however, be expected to be sorbed strongly to the clay particles and the amounts of U(IV) sorbed are expected to be proportional to its concentration in solution, that is determined by the solubility of $UO_2(s)$ in case solubility equilibrium is attained. In case the dissolution rate of $UO_2(s)$ is very low,
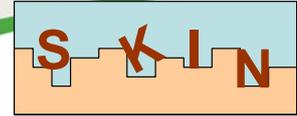
solubility equilibrium will not be attained during the residence time of the clay particles in the canister and the amount adsorbed and transported away will be lower.

Erosion of bentonite in tunnel poses fuel in contact with clay slurry. The amount of uranium transported by bentonite particles is described by equation (1):

$$R_U = [U]_{sol} \cdot q \cdot (1 + C_{Clay} \cdot K_d) \qquad (1)$$

where: q is the flow rate, C_{clay} - clay concentration and $[U]_{sol}$-solubility of U(IV).

A basic assumption of Equation (1) is U dissolution rate from SNF is not so much slower than U sorption on clay, $[U] \approx [U]sol$, the amount U dissolved from SNF and transport via clay slurry should be much faster than the conditions without clay slurry.

If UO_2 dissolution rate is much lower the U(IV)sorption rate, $[U] << [U]_{sol}$ the amount U dissolved from SNF and transport via clay slurry should be much smaller than that at the conditions with near constant solubility level, as assumed in Equation1.

The transport rate of clay slurry is another important factor. The high clay transport rate may result in the increase of the amount of U sorbed on the clay and that dissolved from SNF.

Because of the difficulties in avoiding oxidation while working with $UO_2(s)$, crystalline $ThO_2(cr)$ was used to simulate the fuel $UO_2(s)$ matrix.

The major objective of this work is to investigated in how much degree the presence of clay slurry can affect the Th(IV) concentration in ThO_2 leaching experiment. This information is useful to predict the migration of radionuclides from SNF repository.

Experimental

Methods and materials

There are several difficulties need to overcome:

a) Very low solubility of $ThO_2(cr)$

To get enough Th concentration in solution to study ThO_2 dissolution and Th sorption on clay, we conducted experiment at lower pH conditions, pH 5.5 and pH 3.3. ThO_2
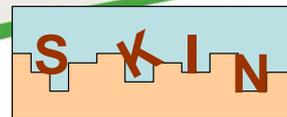
dissolution in solutions with normal groundwater pH (8.2) with and without 2mM NaHCO$_3$ was also investigated.

b) How to separate clay suspending particles from ThO$_2$ particles?

Molecular sieve, i.e. "membrane bag" with pore size 1000-10000 dalton was used to separate clay slurry and ThO$_2$ particles and water solution.

c) Naturally existing clay contains significant Th.

The content of Th in bentonite is ppm level and can disturb Th(IV) sorption experiment. Instead of using naturally existing clay, a synthetic clay, montmorillonite, was manufactured. This clay predominates the BET specific surface areas in bentonite and contains much less Th than the naturally existing bentonite.

Arrangement

The experimental arrangement with two batches is shown in Fig 1. To get rid of suspending ThO$_2$ particles, all solution samples were high-speed-centrifuged. Th concentrations in all samples were analysed by ICP-MS. The detection limit of ICP-MS for Th is about 0.5-1 ppt (10^{-12}).
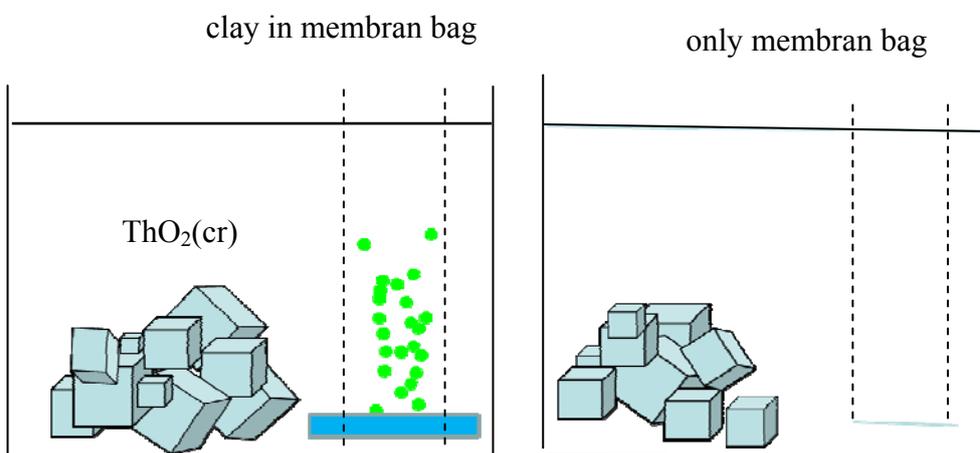

Fig 1. *The arrangement of batch experiments with or without presence of synthesised montmorillonite. (0.25 g) in Membrane bag (1000-10000 Dalton). 0.75g ThO$_2$ (prewashed 3 times with using ultrasonic bath, till clean solution, 430 ml water solution.*
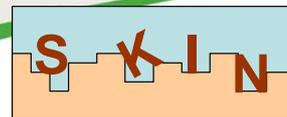
ThO_2 fragments used in the experiment was 0.1 mm sized crystalized ThO_2, pre-rinsed in pH 2.5 solution with using ultrasonic bath and the suspending fine particles were removed. SEM Images of ThO_2 fragments used in the experiments are shown in Fig 2.

The red marks on the top of Fig 3 are the XRD pattern of reference ThO_2. The result of XRD analysis shows the ThO_2 used in this work is a perfectly crystalized ThO_2.

Result and discussion

ThO_2 dissolution and Th(IV) sorption on the clay

The result of experiment at initial pH 3.3 was shown in Fig 4.
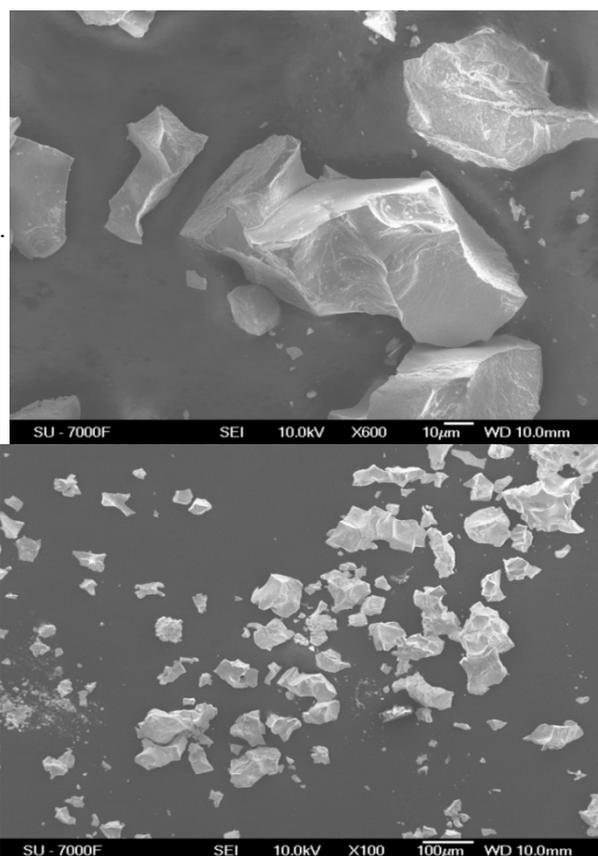

*Fig 2. SEM of ThO_2 fragments used in the experiments*
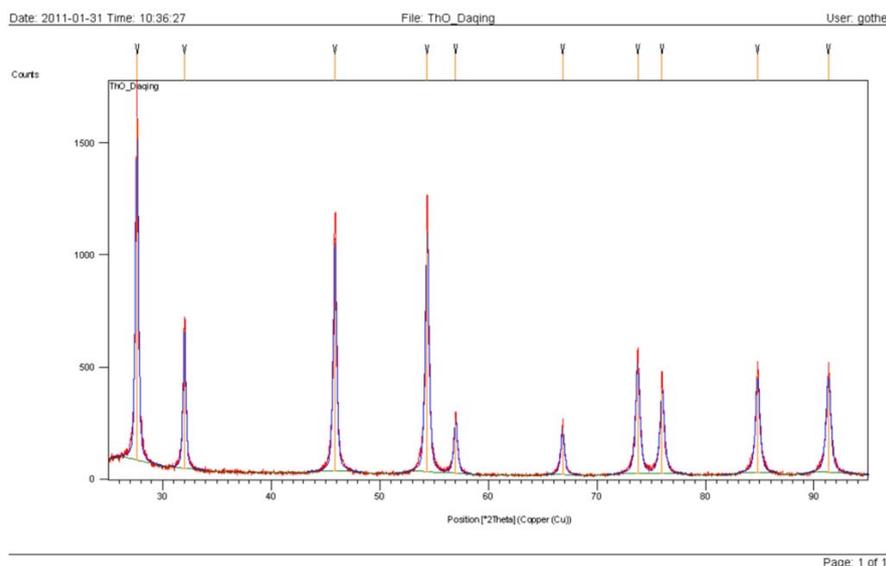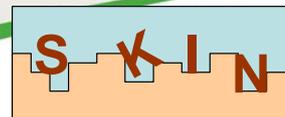
Fig 3. XRD of ThO₂ fragments used in the experiments

The results are summarized below:

1) The experiment was conducted for three months at pH 8.5 without carbonate. The result is not plotted in figure. In the batch a) with presence of clay, Th(IV) concentration is below to the detection limit 0.5 ppt, 0.02 nM and in the batch b) without clay, Th concentration reached 2 ppt after 3 months interaction. This concentration is much much lower than the solubility of ThO_2(cr) at neutral pH that previously reported, 1-10 nM [1]. One reason may be that in the present experiment, all ThO_2 fragments are well crystalized and washed in acidic solution.

2) In the experiment with pH 3.5, free from clay and carbonate, ThO_2 concentration was approaching its solubility level 35 ppt, 0.15 nM, as shown in Fig 4. The present work suggests that the dissolution of ThO_2 is a slow process, the concentration of Th(IV) reached a stable level 35 ppt after one month. In the batch experiment with the presence of clay, Th concentration the Th(IV) is lower than that without clay, due to that the Th(IV) sorption process on clay is much faster process than ThO_2 dissolution fromThO_2. The sorbed Th(IV) on clay at the end of the experiment: dissolving the clay mineral (0.25g) with 19 mL acidic solution, 0.5ml 65% HNO_3 , after shaking for one week, Th concentration in solution is 7 ppt. This result indicates that even at acidic solution (1.5% HNO_3),the Th(IV) dissolved from clay at acidic solution is only 15% of
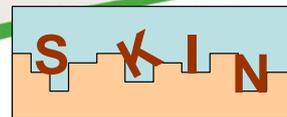
that sorbed on clay during 220 days experiment.. 19ml×7 ppt / (430ml ×20ppt) = 15% it means that the most part of Th(IV) sorbed on the clay cannot be easily desorbed.
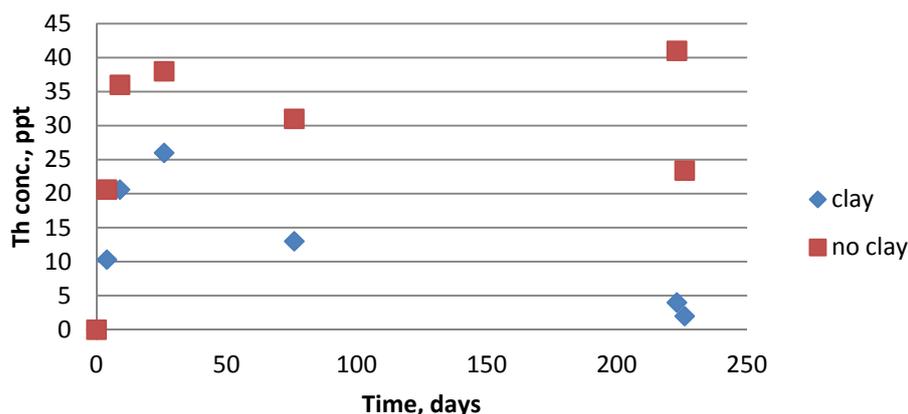

*Fig. 4, Th concentrations in batch experiments with or without clay, initial pH 3.3.*
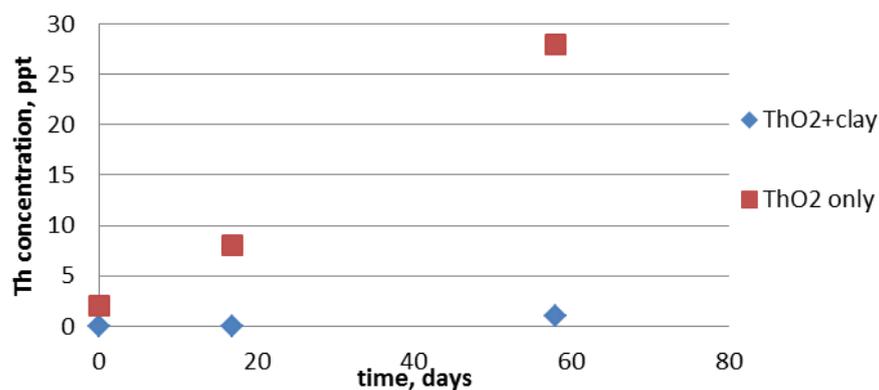
Fig 5. Th concentrations in batch experiments with or without clay, initial pH 5.5. The two batch experiments contain the same amount of ThO₂.

3) At pH 5.5, the sorption of Th(VI) on the clay is much stronger than that at pH 5.5. ThO_2 dissolution is a slow process, Th(IV) concentration increases with reaction time.
It was previously reported that the Th (aq) concentrations for pH > 5 after 10 days of leaching obtained with high fired $ThO_2(cr)$ reach 0.22 nM [2], The result of the present experiment is rather close to this reported data.
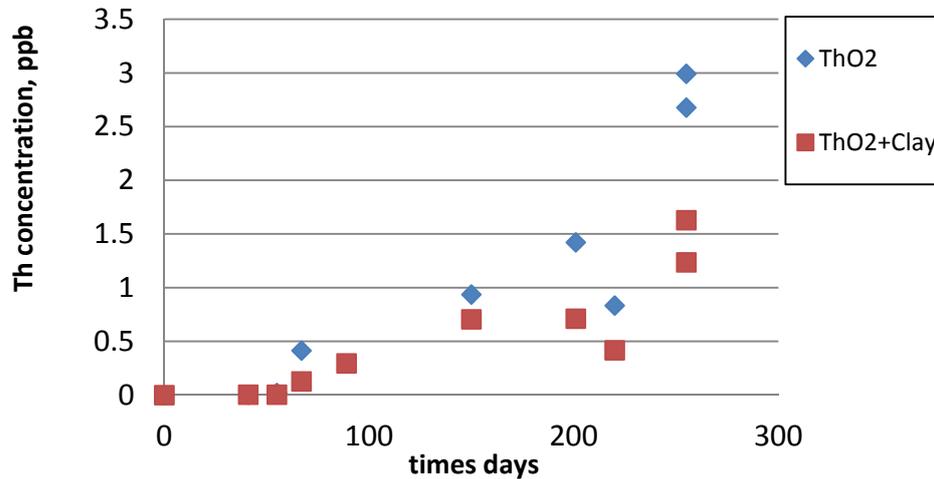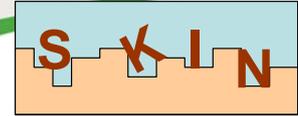
Fig 6. *ThO₂ dissolution in 10mM NaCl and 2mM NaHCO3 solution, pH 8.2*

4) In the batch experiment with solution of 10mM NaCl and 2mM NaHCO₃, Th(IV) concentration is three orders of magnitudes higher than that conducted with carbonate free solution, reached 3 ppb. 1.3×10^{-8} M, which is similar with the reported value in the carbonate containing solution $9.7 \cdot 10^{-9}$ M up to $6.5 \cdot 10^{-7}$ M.

It should be noted that in the batch experiment, NaHCO₃ concentration is similar to that in normal hard rock groundwater, 2mM. The carbonate content in snow is 43 ppm.

Conclusions

From the result discussed above based on the experiments using ThO₂ to simulate UO₂, it can summarized that UO₂(s) dissolution rate can be sufficiently low, so that U(IV) solubility, in the canister void, can not be satisfied during the time of the residence of the clay slurry in the void. In this case, the amount of U(IV) sorbed on clay particles (proportional to sorption coefficient (K_d) and concentration of U(IV) in solution) will be lower than that in a solution with the U(IV) concentration at UO₂ solubility level.

This is clearly seen from the experimental data, where $[Th]_{(ThO2+clay)} < [Th]_{(only\ THO2)}$. Therefore it can be expected that $[U](t)$ should be lower or much lower than $[U]_{(solubility\ of\ UO2)}$ in a very long period of time, even longer than the time of clay staying in SNF canister void. Therefore, we can conclude that the invasion of clay slurry to canister void during the glacial period can enhance the radionuclide migration, but not so much
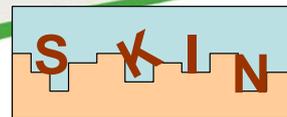
as that conservatively assumed before (Equation1, SKBTR-11-01), because the U concentration in the canister void is lower than the that in clay slurry free conditions. Therefore, we can say that it is not fair to calculate the amount of transported U(IV) by Equation 1 given in the introduction part. This information is useful for the safety assessment.

Future work

The batch experiment with 2mM carbonate will be continued until the Th(IV) reach a stable level. Another new batch experiment under relevant conditions will be conducted to prove the observation made in this work. Under SKB's coordination and support, we will conduct similar experiments in a rather long period of time, to better demonstrate the finding in this work.

Acknowledgement

References

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